Development of Detailed and Reduced Kinetic Mechanisms for Surrogates of Petroleum-Derived and Synthetic Jet Fuels

C.T. Bowman (Stanford University, co-PI)
N.P. Cernansky (Drexel University, co-PI)
F.N. Egolfopoulos (University of Southern California, PI)
R.K. Hanson (Stanford University, co-PI)
C.K. Law (Princeton University, co-PI)
D.L. Miller (Drexel University, co-PI)
H. Wang (University of Southern California, co-PI)

In collaboration with:
W. Tsang & J. Manion (NIST)
T. Lu (University of Connecticut)
A. Violi (University of Michigan)

Phase I: AFOSR Grant: FA9550-08-1-0040 (AFRL Energy-IPT)
Period of performance: 3/1/08 – **11/30/10**

Phase II: AFOSR Grant: FA9550-11-1-0217 (AFRL Energy-IPT)
Period of performance: **9/1/11** – 8/31/14

Objectives - General

- **To understand and quantify the combustion properties of practical fuels used in high-speed air-breathing propulsion systems, which is essential towards the selection of appropriate surrogate fuels.**
- **To provide a roadmap towards the development of kinetic models that are relevant to conditions encountered in high-speed applications.**
- **To address both short-term (current fuels and systems) and potential long-term (fuel-flexible energy conversion and design) needs of air-breathing propulsion, by considering fuels of relevance to:**
  - **conventional petroleum-derived "reference" JP-8;**
  - **non-petroleum-derived jet fuels, e.g. synthetic and/or bio-derived.**

Objectives – Specific (1)

- **To use a variety of experimental and theoretical approaches to tackle the problem of combustion kinetics keeping in mind:**
  - **The molecular structure of the pertinent fuels**
  - **The flow conditions that are expected in high-speed air-breathing propulsion systems**

- **To provide insight into the effects of fuel type and its heating time history and assess thus the validity of basic assumptions behind the choice of kinetic models in turbulent combustion simulations – from very simple to complex, e.g.,**
  - **One step chemistry**
  - **Complex chemistry validated under "normal" laboratory conditions**
  - **Criteria for reducing kinetic models for large fuel molecules**

Objectives – Specific (2)

- **To examine whether current description of the combustion regimes is sufficient and/or complete. Examples of questions to be answered:**
  - **How one can define in general the laminar flame speed (to scale the turbulent flame speed), and in particular for fuels notably more complex than H_2 and CH_4?**
  - **What is the role of fuel decomposition caused by the broadening of the preheat zone and/or by the mixing of reactants with hot combustion products at high levels of turbulence intensity?**
  - **Is there a low-dimensional kinetic space that could be used to describe the rate-controlling chemical processes under conditions of relevance?**
  - **Are there additional parameters that should be considered in regime diagrams, particularly for complex hydrocarbon fuels?**

Jet Fuels Composition (courtesy of Tim Edwards)

	4658	3327	4734	4572	4765	3773	World survey
	Jet A composite blend	JP-7	F-T Jet	RP-1	Coal-based jet fuel DCL	JP-8	Jet A, Jet A-1, JP-8, JP-5, TS-1
Paraffins (*n*- + *i*-)	55.2	67.9	99.7	57.6	0.6	57.2	58.8
Cycloparaffins	17.2	21.2	<0.2	24.8	46.4	17.4	10.9
Dicycloparaffins	7.8	9.4	0.3	12.4	47.0	6.1	9.3
Tricycloparaffins	0.6	0.6	<0.2	1.9	4.6	0.6	1.1
Alkylbenzenes	12.7	0.7	<0.2	2.1	0.3	13.5	13.4
Indanes/Tetralins	4.9	<0.2	<0.2	0.3	1.1	3.4	4.9
Indenes	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Naphthalene	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	0.13
Naphthalenes	1.3	<0.2	<0.2	0.3	<0.2	1.7	1.55
Acenaphthenes	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Acenaphthylenes	<0.2	<0.2	<0.2	0.4	<0.2	<0.2	<0.2
Tricyclic Aromatics	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2

	3638	3602	3642
	Jet A	Jet A	RP-1
Aromatics (ASTM D1319)	12	24	2.9

Phase I (completed): Tasks

- **Experimental:**
  - **Studies of low, intermediate, and high temperature kinetics in flow reactors in shock tubes**
  - **Ignition delays and species time evolution in shock tubes**
  - **Ignition, propagation, and extinction of laminar flames**
  - **Transport coefficients**

- **Theory:**
  - **Detailed kinetic models - JetSurf 2.0 (working model):**
    - **High-temperature kinetics for:**
      - ***n*-alkanes up to C_{12}**
      - ***n*-butyl-cyclohexane**
  - **Transport models with emphasis on long-chain aliphatics**
  - **Model reduction and uncertainty propagation**
  - **Computational flame diagnostics**

Phase I (completed): Parameter Space (1)

- **Fuels:**
  - **Reference Jet-A and JP-8 samples, including low and high aromatic contents**
  - **Fischer-Tropsch and bio-derived jet fuels constituted entirely of *n*- and *iso*-alkanes**
  - **A reference coal-derived jet fuel constituted entirely of cycloalkanes**
  - **$C_{5\text{-}12}$ *n*- and *iso*-alkanes**
  - **$C_{7\text{-}12}$ *cyclo*-alkanes**
  - **Aromatics**
  - **Blends of the selected single-component fuels**

Phase I (completed): Parameter Space (2)

- **Thermodynamic conditions:**
  - **Pressures: 0.25 to 30 atm**
  - **Unburned reactant temperatures: 300 to 1250 K**
  - **Shock tube experimental temperature range: 650 to 2000 K**
  - **Reactant composition: equivalence ratio bracketed by lean and rich flammability limits, typically ranging from 0.5 to 1.5**

Phase I Matrix	C_4-C_{12} *n*-alkanes	*iso*-alkanes	cyclo-alkanes	*n*-alkenes *iso*-alkenes	aromatics	fuel mixtures	jet fuels
Shock tube: Ignition delay, species concentrations	C_5, C_6, C_7, C_8, C_9, C_{12} 0.35 to 34 atm	2,4-DMP 2,5-DMH 2,5-dimethyl-hexane 2,7-dimethyl-octane iso-octane 1-20 atm	cyclo-hexane (CHX) methyl-CHX *n*-butyl-CHX decalin 1-20 atm	reaction rate measurements of OH+alkenes	toluene 1-50 atm (ARO)		JP-8, Jet-A, 20 atm (ARO) JP-7, RP-1 4-40 atm (AFOSR)
Flow reactor at 8 atm: Low-intermediate T; reactivity sweeps and species concentrations	C_7, C_{10}, C_{12}	*iso*-cetane (no reactivity)	*n*-propyl-CHX *n*-butyl-CHX	decalin	*o*-, m-, p-xylene (partially funded by ARO-STIR)	*o*-, *m*-, *p*-xylene+n-C_{12} *iso*-cetane+*n*-C_{10}	Jet-A JP-8 S-8 DCL
Flow reactor: Intermediate-high T; species concentrations	C_7, C_{12} up to 8 atm						
Laminar flame speeds	C_4, C_5, C_6, C_7, C_8, C_9, C_{10}, C_{12} 1-20 atm	*iso*-butane 2- & 3-methyl-heptane 2,5-dimethyl-hexane *iso*-octane 1-10 atm	CHX methyl-CHX ethyl-CHX *n*-propyl-CHX *n*-butyl-CHX CPD 1-20 atm	1-butene 2-butene *iso*-butene 1-10 atm	benzene (B) toluene *n*-propyl-B 1,2,4-TMB 1,3,5-TMB *o*-, m-, p-xylene 1 atm	methyl-CHX+*n*-C_{12} toluene+*n*-C_{12} 1 atm	JP-7 JP-8 S-8 Shell-GTL R-8 1 atm
Flame ignition	C_3,C_4, C_5, C_6, C_7, C_8, C_9, C_{10}, C_{12} 1-3 atm	*iso*-butane 2- & 3-methyl-heptane 2,5-dimethyl-hexane 2,7-dimethyl-octane *iso*-octane, 1 atm	CHX methyl-CHX ethyl-CHX *n*-propyl-CHX *n*-butyl-CHX 1 atm				
Flame extinction (at 1 atm)	C_5, C_6, C_7, C_8, C_9, C_{10}, C_{12}		CHX methyl-CHX *n*-butyl-CHX CPD		benzene, toluene *n*-propyl-B 1,2,4-TMB 1,3,5-TMB *o*-, m-, p-xylene		JP-7 JP-8 S-8 Shell-GTL R-8
Detailed kinetic models	JetSurf 1.0, 2.0		JetSurF 2.0	JetSurF 2.0 (*n*-alkenes)	JetSurF 2.0 (benzene & toluene)		semi-empirical with USC Mech II (STTR)
Transport properties	C_3-C_8 exp. & MD	empirical estimates	empirical estimates	empirical estimates	empirical estimates	empirical estimates	empirical estimates
Model reduction	lumped+skeletal (USC	*iso*-octane (LLNL)	skeletal *n*-butyl-CHX		skeletal toluene (JetSurf 1.1)	skeletal *n*-C_{12}+*n*-butyl-	

Phase II: Tasks (1)

- **High Re number, turbulent premixed jet flames:**
  - **Re ~ O(10^5) or higher**
  - **Use of conventional and high-speed diagnostics**
  - **Study of simple and complex large MW fuels – emphasis on isomers**
  - **Correlation of experimental observations to what is known at the flamelet level**

- **Quantification of effects of fuel cracking on local flame properties:**
  - **Use PDFs of preheat zone temperatures from high-resolution computations and/or measurements of high Re turbulent flames**
  - **Assess effects of burned-unburned mixing in the "free stream" on the flame response**
  - **Use detailed simulations to search for a low-dimensional kinetic space that could be used to describe the rate-controlling chemical processes**
  - **Use of the composition of multicomponent, partially reacted mixtures as an additional set of independent variables in the jet fuel surrogate definition, which will lead to JetSurF 2.5 as an end-goal of the current Energy-IPT project.**

Phase II: Tasks (2)

- **Studies of fundamental flame properties of products of fuel decomposition:**
  - **The results of the fuel cracking studies in the preheat zone and free stream will be used as input**
  - **Existing and new experimental approaches will be implemented to measure such properties for multicomponent smaller MW fuels under conditions of relevance**

- **Shock tube studies of fuel pyrolysis and oxidation:**
  - **Existing and new experimental techniques will be used to identify pathways of fuel pyrolysis and oxidation of jet fuels surrogates**
  - **Special emphasis on:**
    - **formation and consumption of radical species**
    - **the rate of change of chemical energy during reaction**
    - **the fuels behavior under variable heating profiles**

Phase II: Tasks (3)

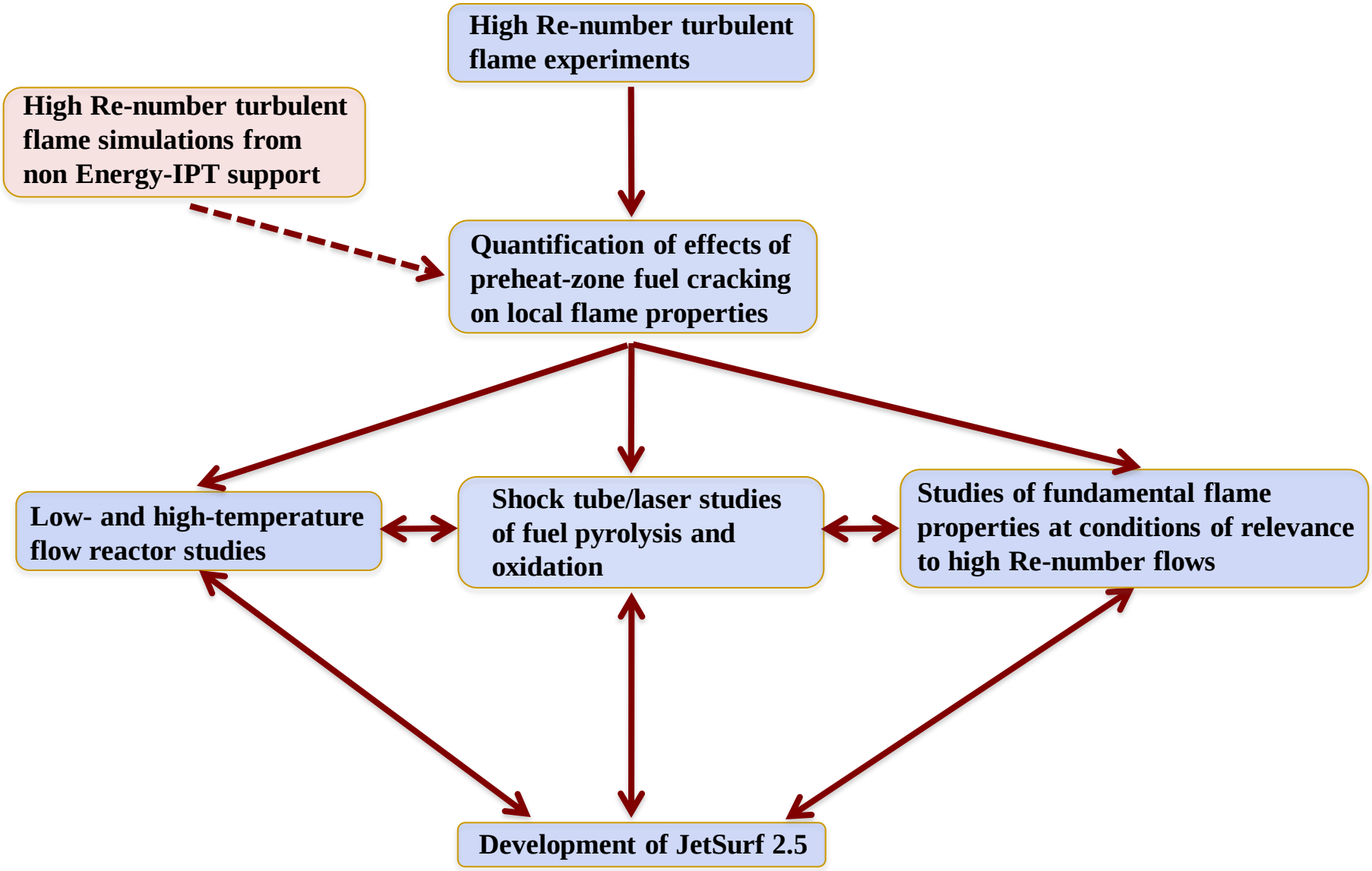
- **Low- and high-temperature flow reactor tube studies of fuel pyrolysis and oxidation mimicking the conditions of the preheat zone:**
  - **High temperatures will dominate the initial fuel decomposition**
  - **Lower temperatures regimes are expected to be important in locations close to the fuel injection region**
  - **Time scales of lower temperature experiments could be accelerated through the use of additives**

- **All results obtained in aforementioned Tasks will be used to guide and assess the validity of the approaches involved in the development of the JetSurf 2.5 kinetic model.**

Phase II: Fuels

- **Relevant to:**
  - **petroleum-derived JP-8 (~ $C_{11}H_{21}$);**
  - **synthetic JP-8, e.g. S-8 (~ $C_{10}H_{22.7}$);**
- **Focus on:**
  - ***n*-dodecane (representative *n*-alkane);**
  - ***n*-butyl-cyclohexane (representative *cyclo*-alkane);**
  - **2,7-dimethyl-octane (representative *iso*-alkane);**
  - ***n*-propyl-benzene (representative aromatic);**
  - **binary and tertiary mixtures of the selected neat fuels;**
- **Additional neat fuels of similar MWs and chemical classifications will be considered during the model development stage to assure chemical consistency of the kinetic model.**

Block Diagram of Energy-IPT Program



Energy-IPT Presentation Schedule

8:15-8:30	Program Overview (Egolfopoulos; University of Southern California)
8:30-9:00	Low/Intermediate Temperature Flow Reactor Studies (Cernansky & Miller; Drexel University)
9:00-9:45	Intermediate/High Temperature Flow Reactor and Shock Tube Studies (Bowman & Hanson; Stanford University)
9:45-10:15	Flame Studies of Jet Fuels and Surrogate-Related Hydrocarbons (Egolfopoulos; University of Southern California)
10:15-10:45	Break
10:45-11:15	Flame Kinetics of Surrogate Jet Fuel Components (Law; Princeton University)
11:15-11:50	Reaction Kinetics of Jet Fuels (Wang; University of Southern California)
11:50-12:00	Summary